

PCT

e street to over

......

WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



(51) International Patent Classification ⁵ :		(11) International Publication Number: WO 94/21769
C11D 1/66	A1	(43) International Publication Date: 29 September 1994 (29.09.94)
(21) International Application Number: PCT/SE (22) International Filing Date: 10 March 1994 (BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL,
(30) Priority Data: 9300954-6 23 March 1993 (23.03.93)	s	Published With international search report.
 (71) Applicant (for all designated States except US): NOBEL AB [SE/SE]; S-444 85 Stenungsund (SE). (72) Inventor; and (75) Inventor/Applicant (for US only): JOHANSSON, [SE/SE]; Bogärdesgatan 8, S-416 54 Göteborg (SE). (74) Agent: ANDERSSON, Rolf; Berol Nobel AB, S. Stenungsund (SE). 	Ingegär !).	d · · · · · · · · · · · · · · · · · · ·
(54) Title: ALKYL GLUCOSIDE, ITS USE FOR CLEAN (57) Abstract	ING P	urpuses, and cleaning composition
In an alkyl glucoside of the formula (I): RCH ₂ O(G) _x	H, R is	an alkyl group having a total of 8-12 carbon atoms and containing 2-4
groups of formula -CH(CH ₃)- in its carbon chain: G is a more	osacch	aride residue; and x is 1-4. The use of the alkyl glucoside as a surfactant containing an alkyl glucoside of formula (I), a complexing agent and a

ME STEEL STATES OF TANKE OF STATES

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
ΑŬ	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE.	
BE	Belgium	GR	Greece	NL	Niger
BF	Burkina Paso	HU	Hungary		Netherlands
BG	Bulgaria	Œ	Ireland	NO	Norway
BJ	Benin	TT.	Italy	NZ	New Zealand
BR	Brazil	ĴР	Japan	PL	Poland ·
BY	Belarus	KE	Кепуа	PT	Portugal .
CA	Canada	KG	•	RO	Romania
CF	Central African Republic	KP	Кутдувал	RU	Russian Federation
CG	Congo	M.P	Democratic People's Republic	SD	Sudan
CB	Switzerland	***	of Korea	SE	Sweden
CI	Côte d'Ivoire	KR	Republic of Korea	SI	Slovenia-
CM	Cameroon	KZ	Kazakhstan	SK	Slovakia
CN		ц	Liechtenstein	SN	Senegal
	China	LK	Sri Lanka	TD	Chad
cs	Czechoslovakia	LU	Luxembourg	TG	Togo
CZ	Czech Republic	LV	Latvia	ΤĴ	Tajikistan
DE	Germany	MC	Monaco	TT	
DK	Denmark	MD	Republic of Moldova	UA	Trinidad and Tobago
ES	Spain	MG	Madagascar		Ukraine
FI	Finland	ML	Mali	US	United States of America
FR	France	MIN	Mongolia	UZ	Uzbekistan
GA	Gabon	IVE	ModRoff	VN	Vict Nam

ALKYL GLUCOSIDE, ITS USE FOR CLEANING PURPOSES, AND CLEAN-

This invention relates to an alkylaglucoside in which the alkylaglucoside in which the alkylaglucoside as methyl-branched mas well asothed use of the alkylaglucoside as a surfaces. The invention also concerns accidening that a solubiliser and preferably also with a solubiliser.

a solubiliser and preferably also with and complexing agent. 10 In recent years attention has focused on alkyl glucosides since these have proved to be more seasily biodegradable than other non-ionic surfactants, such as ethylene oxide adducts of fatty alcohols. US Patent Specifica-HOUSE NE tion 3,839,318 thus describes the production of alkyl glu-715 M cosides and alky Foligosaccharides, such as n-octyl gluco-A Sie side an-hexyliglucoside, n-decyliglucoside, n-dodecyl glucoside, isodecyl glucoside, isoundecyl glucoside, isotriand accept glucoside and the corresponding oligosaccharides. The United States Stationary Invention Registration H171 20 states that alkyl glucosides of formulae R(OG) and R(OG), are excellent suffactants. In these formulae, R is an the stalkylpor alkenylegroup which is branched at the second Asscarbongatom or at adhigher carbon atom, the branch being To the selected from the group methyl, ethyl, isopropyl, n-pro-25 pyl, butyl, pentyl, hexyl and mixtures thereof, provided thateR contains from about 7 to about 30 carbon atoms: ent of G. is absaccharide group selected from the group glucose, fructose, mannose, galactose, talose, allose, altrose, idose, arabinose, xylose, lyxose, ribose and mixtures 30 thereof; and x is 2 or more. Example 1 contains a description of the production of two product mixtures substantially made up of 2-ethylhexyl glucoside and isooctyl glucoside, respectively.

DE 20 36 472, EP 306 650, EP 306 651 and EP 366 652, 35 inter alia, also describe alkyl glucosides.

15

35

Even though alkyl glucosides generally are easily biodegradable, they are only used to a limited extent in many ranges of application, such as the cleaning of hard surfaces, since they are too high-foaming and/or have too poor a cleaning power. It is therefore a desideratum to provide non-ionic surfactants which are about as easily biodegradable, but which have a better cleaning effect on hard surfaces and/or are more low-foaming than known alkyl glucosides.

According to the present invention, it has now surprisingly been found that an alkyl glucoside of formula

RCH₂O(G) H (I) \mathbf{x}

wherein R is an alkyl group having a total of 8-12 carbon atoms and containing 2-4 groups of formula -CH(CH₃)- in its carbon chain, G is a monosaccharide residue, and x is 1-4, is advantageously used as a surfactant in compositions for cleaning hard surfaces. The alkyl glucoside of formula I shows good cleaning and wetting properties, as well as low foaming compared with other alcohols of approximately the same chain length. In addition, the alkyl glucoside has proved to be easily degradable and have low biotoxicity. Tests have not shown any skin irritations caused by the alkyl glucosides. Preferably, there are 2 or 3 methyl groups. Compounds in which R contains 9 or 10 carbon atoms and x is 1 or 2 are especially preferred, having a good cleaning power and being comparatively easy to produce.

The compounds according to the invention can be produced in conventional manner by reacting an alcohol of formula

RCH₂OH (II)

wherein R is as indicated above, with a monosaccharide in the presence of an acid catalyst, the molar ratio of the alcohol to the monosaccharide being 2:1-80:1. The catalyst may be an inorganic or organic acid. The reaction is per-

formed under vacuum at 90-120°C for about 1-4 h. Conveniently, the resulting reaction mixture is first filtered and then neutralised with an organic and or an inorganic Stare base ty whereupon excess alcohol is a carefully removed e.g. The transfer of the temporal property of the second property of the and about are The alcohols of formula (A) Jean she produced in conwentional manner by condensing propene, butene or mixtures. whereuponatheadie, striegoratetramers obtained mare prolonged with a carbon atomaby the oxoprocess. The 10 resulting aldehydes may then measily be converted to the dala corresponding alcohols Theralcohols robtained form a complex mixture of methyl-branched structures balthough some ethyl substituents may be present The amount of quaternary carbon found in the carbon chain is very small, and 15. alcohols containing quaternary carbon are to be regarded as impurities not encompassed by the invention. Examples of suitable alcohols are Exxal 9, Exxal 10, Exxal 11. Exxal 12 and Exxal 13, all sold by Exxon Chemical. The monosaccharides used as reactant suitably consists of pen-20 tose and hexose. Specific examples of monosaccharides used in the production of the inventive glucosides are glucose, _____mannose, galactose, otalose, mallose, altrose, idose, arabinose xylose ribose and lykose Glucose is usually preferred for commercial reasons to , as we see , we compare 25 The alkyl glucosides according to the invention are suitable for useding compositions for cleaning hard sur-

faces, e.g. for degreasing such surfaces or washing up. Excellent results are obtained in the degreasing of lacquered or unlacquered metal surfaces. Apart from the

30 inventive alkyl glucoside, these compositions preferably contain a water-soluble solubiliser and suitably contain a complexing agentary where person of the last

Examples of solubilisers are alkyl ether polyalkylene glycol, such as monobutyl diethylene glycol; glycols, such 35 as diethylene glycol, dipropylene glycol and propylene glycol; alcohols, such as ethanol, propanol and isopropanol; alkyl glucosides in which the alkyl group has

WO 94/21769 PCT/SE94/00198

4-8 carbon atoms; and/or tertiary or quaternary amine alkoxylates in which the alkyl group, which may be straight or branched; saturated or unsaturated, has 8-20 carbon atoms and in which:6-30 mol of alkylene oxide is 5 added per mol of amine Preferably, 50-100 mol per cent of the added alkylene oxide consists of ethylene oxide, the remainder preferably consisting of propylene oxide or a mixture of propylene oxide and butylene oxide. The different alkylene coxides can be added randomly or in blocks. 10 If the cleaning composition should be exceptionally lowfoaming, the alkylene oxide chain conveniently ends with an addition of 1-5 mol of propylene oxide and/or butylene oxide. The ratiosof the solubiliser to the inventive alkyl glucoside is usually 1:10-5:1, preferably 1:3-3:1.

The complexing agent may be a conventional inorganic or organic agent, such as an inorganic phosphate or NTA, EDTA, citric acid or a polycarboxylate. The amount added may vary from nothing at all to 300% by weight of the inventive alkyl glucoside. Preferably, the quantitative 20 ratio of the complexing agent to the alkyl glucoside is 1:10-2:1.

The cleaning compositions may further contain other additives, such as pH-adjusting agents; antifoaming agents, enzymes, other surfactants and scents. The com-25 positions are usually aqueous and in the form of emulsions, microemulsions or solutions.

The invention will now be further illustrated by a few Examples.

. Example 1

15

35

An alkyl glucoside was produced by reacting 2.6 mol 30 of an alcohol (Exxal 9) of formula (II), wherein R is a C_8 alkyl having a methyl substitution of about 2 (average value), with 0.4 mol of glucose in the presence of 0.015 mol of sulphuric acid as catalyst at 110°C and 70 mbar. 35 The reaction was interrupted after 105 min. The resulting product mixture was treated by distilling off excess alcohol under vacuum. The yield was 105 g, consisting of 60%

of C_q -branched alkyl monoglucoside, 15% of C_q -branched -alkyl diglucoside and a residue of higher oligomers. The glucosides had an average degree of polymerisation (DP) of about 1.5. The structure was determined by gas chromato-5 graphy, mass spectrometry and NMR.

Ah alkyl glucoside wassproducedeby reacting 7.6 mol of an alcohol (Exxal 10) of formula (11) 9 wherein R is a Co alkyl having a methyl substitution of about 2.2 10 (averageavalue), with 1.2 mol of glucose in the presence of 0:015 mol of sulphuric acid as catalyst at 90-111°C and 100 mbar. The reaction was interrupted after 120 min. The reaction mixture was treated by distipling off excess alcohol under high vacuum. The yield was 278 g, consisting 15 of 60% of monoglucoside, 12% of diglucoside and a residue of higher oligomers. The glucosides had an average DP of 1.6.8 8 8 8 8 8 8 8 8 8 8 Example 3 a company

Here, 20 ml of each of the cleaning compositions below, diluted with 10 parts by weight of water per part by weight of the composition, was applied on a vertically arranged iron sheet soiled with mineral oils, soot, salts and clay. After application, the coated surface was rinsed with water without any mechanical treatment. ស្តាស់ ស្ត្រាស់ ស្ត្រាស់ សង្គ្រាស់ សង្គ្រា

ELECTION OF THE PROPERTY OF THE WAS ASSESSED.

Fred & Power of the Bridge

'*•	Components	Со	mpos	itio	n, 8	by.	weig	ht
5	British States	100 100	2	A ∷	В	С	D	E
	Glucoside (Example 1)	· 5-	4.4					
a :.	Glucoside (Example 2)		5	y -2	8. 1	٠.,	4.5	
<u>.</u>	gGlucosidecA eletra este il	1	1 12	5.	6. 9	454.5	(6.1	
. 10	Glucoside, Bo to dom to	;	. 12 .	216.2	5.5	y" vr		
	Glucoside C	•	100	W 1	z.n - 7	:5℃	200	ł
	Glucoside D	ta A	1. 47	1 165		1257	5	
:.·.(%)	Butyldiethylene glycol	· 5 · · ·		11 6	11 0	11	11	111
	Quaternary ethoxy-			1 41	A. L.	et.	į.	
15	lated fatty amine		37;		v 11	119	,	
	(Berol 555)	. 4 .	4.:			$\gamma_1 \circ r_2$	3 O.	
	NTA	5	5	3	3	3	3	5
	Water	86	86	81	81	81:	81	84

. **20**

Glucoside A = 2-ethylhexyl-O(G)_xH Glucoside B = isooctyl-O(G) H
Glucoside C = n-dodecyl/n-tetradecyl glucoside (APG-600,

Henkel)

and the second of the second of the second

Glucoside D = n-decyl glucoside (Lutensol GD-70, BASF) 25 wherein G = glucoside residue and x = 1.5 (average value).

The attained cleaning effect was assessed with respect to the area of the cleaned surface, as well as its actual cleanness, the figure 1 indicating no improvement and the figure 10 indicating a perfectly clean surface. The following results were obtained.

			<u> </u>
1. M. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1.		Cleaned surface; cm.	<i>"</i>
5. 5.	s koos, en 🔁 mai juiti.	one cas 112 ; service significant service significant service) 46. 17 6 -0 mp
		jang I dilik dikang Igili O Tekna promensa mon	ni calvad
10	B C	80 48	4 6
	D E	72 0	6 1

The foaming of the different ready-to-use solutions was measured according to Ross-Miles ASTM D 1173-53. The following results were obtained.

20	Composition	Foam height, mm			
	Composition	Instantaneously	After 5 min		
	. 1	5	0		
25	2	8	0		
2.5	A	7	0		
	В	20	3		
	С	67	63		
	. D	46	. 45		
30					

WO 94/21769 PCT/SE94/00198

It is evident from these results that the alkyl glucosides according to the invention show an excellent cleaning power and are clearly superior to alkyl glucosides having a straight carbon chain with 10-14 carbon atoms, while at the same time having an acceptable degree of foaming. The composition containing alkyl glucosides having an alkyl group with 8 carbon atoms showed an unsatisfactory cleaning power.

WO 94/21769 PCT/SE94/00198

ing. Nga paling a mangangan palingga kalang at kalang ang kalang at kalang at kalang at kalang at kalang at kalang

ായി. അത്രേ**പ് എട്ടിന്റ**്ടെ സംവിത്യന്ത്ര അവ വരു വഴിച്ച വരു വിരുന്ന വ

. Almant Tirkewing of the Alemand, lights and the light

1. The use of an alkyl glucoside of the general for-5 mula Region 198

 $m_{\rm CDM} \approx 2.1$ -8 30 RCH20(G) $_{\rm H}$) that quote lysts as -8 . A absymptone of $-(\sqrt{8})$ Fig. where -6 equote -6 galaterness bas smooth

- wherein Reis and alkylogroup having a total of 8-12 carbon atoms and containing 2-4 groups of formula -CH(CH3) in its carbon chain; G is a monosaccharide residue; and x is 1-4, as a surfactant for cleaning hard surfaces.
 - 2. Use as set forth in claim 1, characterised in that R is an alkyl group having 9 or 10 carbon 15 atoms.
 - 3. Use as set forth in claim 1 or 2, character is ed in that R has a methyl substitution of 2 or 3.
 - 4. Use as set forth in claim 1, 2 or 3, charac20 terised in that G is a glucose residue.
 - 5. Use as set forth in any one of claims 1-4, characterised in that x is 1 or 2.
 - 6. Use as set forth in claims 1-5 of the alkyl glucoside of formula (I) as a surfactant in a cleaning composi-
 - 25 tion for degreasing lacquered or unlacquered metal surfaces.
 - 7. A cleaning composition, characterised in that it contains, in addition to the alkyl glucoside of formula (I), a water-soluble solubiliser and, optionally, an organic or inorganic complexing agent.
 - 8. A cleaning composition as set forth in claim 7, c h a r a c t e r i s e d in that the solubiliser consists of alkyl ether polyglycols, glycols, alcohols and/or tertiary and/or quaternary alkylamine alkoxylates.
 - 9. A cleaning composition as set forth in any one of claims 6-8, characterised in it contains a solubiliser in an amount of 1:3-3:1 based on the weight of

WO 94/21769 PCT/SE94/00198

10

the alkyl glucoside, and a complexing agent in an amount of 1:10-2:1 based on the weight of the alkyl glucoside.

10. An alkyl glucoside of the general formula .

 $5 \qquad \text{RCH}_{2}O(G)_{x}H \qquad (1)$

wherein R is an alkyl group having a total of 8-12 carbon atoms and containing 2-4 groups of formula -CH(CH₃)- in its carbon chain; G is a monosaccharide residue; and x is 1-4.

•

20

25

30

35

:

International application No.

PCT/SE 94/00198

	الرابة يواف شاء مد يومنسها من أيماني الرابيات الماليات الم	FC1/3E 94/0	<u> </u>
A. CLAS	SIFICATION OF SUBJECT MATTER		r (113)
	(A)		•
	11D 1/66. o International Patent Classification (IPC) or to both r	national classification and IPC	
	DS SEARCHED TO SEARCHED		1
	ocumentation searched (classification system followed b	by classification symbols)	
	11D, C07H		
Documenta	tion searched other than minimum documentation to th	e extent that such documents are included in	n the fields searched
SE,DK,F	I,NO classes as above		•
Electronic d	ata base consulted during the international search (nam	e of data base and, where practicable, search	terms used)
			} .
	•		•
C. DOCL	MENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where ap	oppopriate, of the relevant passages	Relevant to claim No.
		• • • • • • • • • • • • • • • • • • • •	
A	US, A, 3839318 (RICHARD C. MANSF 1 October 1974 (01.10.74)	FIELD),	1-10
	(020200.)		
	. 		
Δ	DE, B2, 2036472 (ATLAS CHEMICAL	INDUSTRIES INC)	1_10
. ^	7 December 1978 (07.12.78)	INDUSTRIES INC.),	1-10
	•		:
i	·	*	:
		,	;
	·		
		·	
			1
	•		
			4 !
			;
		_	
			,
Furth	er documents are listed in the continuation of Bo	x C.	•
-	categories of cited documents: · nt defining the general state of the art which is not considered	"T" later document published after the inte- date and not in conflict with the applic	ation but cited to understand
to be of	particular relevance	the principle or theory underlying the i	
	ocument but published on or after the international filing date nt which may throw doubts on priority claim(s) or which is	"X" document of particular relevance: the considered novel or cannot be considered.	raimed invention cannot be red to involve an inventive
cited to	establish the publication date of another citation or other reason (as specified)	step when the document is taken alone "Y" document of particular relevance: the o	
	nt referring to an oral disclosure, use, exhibition or other	"Y" document of particular relevance: the c considered to involve an inventive step combined with one or more other such	when the document is
"P" docume	nt published prior to the international filing date but later than	being obvious to a person skilled in the	art :
	nity date claimed	'&' document member of the same patent i	
Date of the	actual completion of the international search	Date of mailing of the international se	earch report
29 June	1994	08 -07- 1994	:
	mailing address of the ISA/	Authorized officer	
Swedish F	Patent Office		
	S-102 42 STOCKHOLM	Dagmar Järvman	İ
racsimile N	Jo. + 46 8 666 02 86	Telephone No. + 46 8 782 25 00	i

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

28/05/94 | PCT/SE 94/00198

	document arch report	Publication date		blication date
US-A-	3839318	01/10/74	NONE	
DE-B2-	2036472	07/12/78	FR-A- 2055596 07/05/ GB-A- 1277516 14/06/ US-A- 3772269 13/11/	72 -

Form PCT/ISA/210 (patent family annex) (July 1992)